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(54) ELECTROLESS COPPER PLATING BATH

(57) Abstract:

PURPOSE: To reduce the danger of work as well as to inhibit abnormal deposition by using thiourea as a complexing agent and trivalent Ti ions as a reducing agent in the compsn. of a plating bath.

CONSTITUTION: In an electroless copper plating bath contg. a copper salt, a complexing agent, a pH adjusting agent and a reducing agent, thiourea or its deriv. is used as the complexing agent and trivalent Ti ions are used as the reducing agent. Since the thiourea used as the complexing agent coordinates tightly with Cu ions and can form a stable complex, the electroless copper plating bath is made stable and less liable to decomposition. Since

trivalent Ti ions are used as the reducing agent, the generation of hydrogen is prevented in a plating reaction and this reaction is allowed to take place in the weakly acidic region to neutral region.

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(54) 【発明の名称】 無電解銅めっき浴

(57) 【要約】

【目的】 異常析出が少なく、作業上の危険性も低い無電解銅めっき浴を提供する。

【構成】 銅塩、錯化剤、pH調整剤および還元剤を含む、無電解銅めっき浴において、錯化剤としてチオ尿素またはその誘導体を用い、還元剤として3価のチタンイオンを用いる。

【特許請求の範囲】

【請求項 1】 銅塩、錯化剤、pH調整剤および還元剤を含む、無電解銅めっき浴において、前記錯化剤はチオ尿素またはその誘導体を含み、前記還元剤は 3 価のチタンイオンを含むことを特徴とする、無電解銅めっき浴。

【発明の詳細な説明】

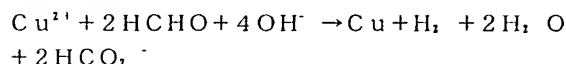
【0001】

【産業上の利用分野】この発明は、無電解銅めっき浴に関するもので、特に、このようなめっき浴に含まれる還元剤の改良に関するものである。

【0002】

【従来の技術】無電解めっきにより銅皮膜を析出させるためのめっき浴は、主として、銅塩と、酒石酸やエチレンジアミンテトラ酢酸 (EDTA) のような錯化剤と、アンモニウム塩や水酸化ナトリウムのような pH調整剤と、ホルムアルデヒドのような還元剤とを含み、その他、浴安定剤や光沢剤の微量添加物を含んでいる。

【0003】上述したように、還元剤としては、ホルムアルデヒドが通常用いられているため、無電解めっき反応は、次式：



に示すように、水素発生反応である。

【0004】

【発明が解決しようとする課題】上述したようにホルムアルデヒドを還元剤とする無電解めっき反応は、水素発生反応であるため、発生した水素が活性化処理されていない部分に吸着することによりめっき成長を促す、といった、いわゆる異常析出が生じやすい。そのため、このような無電解めっきが、たとえば回路基板上の導電パターンの形成に適用された場合、パターンの精度の低下やパターン間の不所望な短絡等の不具合を引き起こすことがある。

【0005】また、還元剤としてホルムアルデヒドを用いる場合、めっき浴の pH 値が高くなると、めっき反応が起こらないため、めっき浴は強アルカリ液となってしまう。そのため、めっき作業をするとき、めっき液が衣服や手に付いたり、また、誤って眼に入ったりするといった危険が伴い、さらに、ホルムアルデヒドの刺激臭が問題になったりしている。

【0006】それゆえに、この発明の目的は、上述したような異常析出を抑制することができ、また、作業上の危険性の低い無電解銅めっき浴を提供しようとするものである。

【0007】

【課題を解決するための手段】この発明は、銅塩、錯化剤、pH調整剤および還元剤を含む、無電解銅めっき浴に向けられるものであって、上述した技術的課題を解決するため、錯化剤がチオ尿素またはその誘導体を含み、

還元剤が 3 価のチタンイオンを含むことを特徴としている。

【0008】

【作用】この発明において、錯化剤として用いられるチオ尿素またはその誘導体は、銅イオンと強く配位して、安定な錯形成を行なうことができる。そのため、無電解銅めっき浴が安定となり、分解が生じにくくなる。

【0009】また、還元剤として 3 価のチタンイオンを用いるため、めっき反応において水素発生がなくなり、また、pH 値についても、弱酸性から中性領域においてめっき反応を生じさせることができる。

【0010】

【発明の効果】したがって、この発明によれば、上述したように、めっき反応において水素発生がないため、異常析出がほとんど生じない。そのため、無電解銅めっきによって、たとえば回路基板上の導電パターンを高い精度をもって形成することができ、また、不所望な短絡等の不具合を引き起こすことを防止でき、それゆえ、微細な導電パターンにも対応できるようになる。

【0011】また、めっき浴の pH 値が弱酸性から中性領域であるため、アルカリ性雰囲気下にも、問題なく無電解銅めっきを適用することができるとともに、作業上においても危険性を低減できる。

【0012】なお、この発明に係る無電解銅めっき浴を用いて実施した無電解めっきにより得られた銅皮膜の密着性や導電率等の特性については、従来のめっき浴による銅皮膜とほとんど差がないことが実験により確認されている。

【0013】

【実施例】次のような組成の無電解銅めっき浴を調製した。

【0014】

クエン酸 3 ナトリウム塩	: 0.34 mol/l
EDTA・2 ナトリウム塩	: 0.08 mol/l
ニトリロ三酢酸	: 0.20 mol/l
塩化銅	: 0.008 mol/l
チオ尿素	: 0.032 mol/l
三塩化チタン	: 0.04 mol/l

このめっき浴を、28%アンモニア水で pH 5.0 に調整し、40℃の条件で、1時間のめっき処理を、SnCl₂ 溶液と PdCl₂ 溶液とによる活性化処理を済ませたアルミナ基板に対して行ない、このアルミナ基板上に約 0.8 μm の銅めっき皮膜を析出させた。この銅めっき皮膜には、異常析出がほとんど認められず、また、その密着性や導電率についても、従来のめっき浴によるものとはほぼ同等の結果が得られた。

【0015】なお、めっき浴の pH 値が、3.0~7.0 の範囲内において特に好ましいめっき操作を行なうことができたが、この範囲外、たとえば pH 2.5 では、析出速度が遅く、十分なめっき皮膜が得られず、また、

pH 7. 5 では、めっき浴が不安定となり、めっき浴中に銅粉末が生成してしまうことがあった。しかし、これらの問題点は、浴温や浴組成を操作することにより、若干解決することができる。

【 0 0 1 6 】 上述した実施例では、錯化剤として、チオ尿素 $\text{CS}(\text{NH}_2)_2$ を用いたが、たとえばテトラメチルチオ尿素 $(\text{CH}_3)_4\text{NCSN}$ 、 $\text{NCSN}(\text{CH}_3)_3$ 等の誘導体を用いても、同等の効果が得られた。

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DOCUMENT-IDENTIFIER: JP 06340979 A

TITLE: ELECTROLESS COPPER PLATING BATH

PUBN-DATE: December 13, 1994

INVENTOR-INFORMATION:

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MURATA MFG CO LTD

COUNTRY

N/A

APPL-NO: JP05130373

APPL-DATE: June 1, 1993

INT-CL (IPC): C23C018/40

ABSTRACT:

PURPOSE: To reduce the danger of work as well as to inhibit abnormal deposition by using thiourea as a complexing agent and trivalent Ti ions as a reducing agent in the compsn. of a plating bath.

CONSTITUTION: In an electroless copper plating bath contg. a copper salt, a complexing agent, a pH adjusting agent and a reducing agent, thiourea or its deriv. is used as the complexing agent and trivalent Ti ions are used as the reducing agent. Since the thiourea used as the complexing agent coordinates tightly with Cu ions and can form a stable complex, the electroless copper plating bath is made stable and less liable to decomposition. Since trivalent Ti ions are used as the reducing agent, the generation of hydrogen is prevented in a plating reaction and this reaction is allowed to take place in the weakly acidic region to neutral region.

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DERWENT-ACC-NO: 1995-064027

DERWENT-WEEK: 200206

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TITLE: Electroless copper@ plating bath - contains copper salt,
chelating agent, pH regulator and reducing agent

PATENT-ASSIGNEE: MURATA MFG CO LTD[MURA]

PRIORITY-DATA: 1993JP-0130373 (June 1, 1993)

PATENT-FAMILY:

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JP 3243889 B2	January 7, 2002	N/A	002	C23C 018/40

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PUB-NO	APPL-DESCRIPTOR	APPL-NO	APPL-DATE
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JP 3243889B2	Previous Publ.	JP 6340979	N/A

INT-CL (IPC): C23C018/40

ABSTRACTED-PUB-NO: JP 06340979A

BASIC-ABSTRACT:

Electroless Cu-plating bath contains Cu-salt, chelating agent, pH regulator, and reducing agent, in which thiourea or its derivs. are used as the chelating agent, and Ti(3+) ions are used as the reducing agent.

USE - Used for electroless Cu-plating, having less abnormal deposition of Cu, and harmless in operation.

CHOSEN-DRAWING: Dwg.0/0

DERWENT-CLASS: M13

CPI-CODES: M13-B;

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PAT-NO: JP02000355774A

DOCUMENT-IDENTIFIER: JP 2000355774 A

TITLE: PLATING METHOD AND PLATING SOLUTION PRECURSORY USED THEREFOR

PUBN-DATE: December 26, 2000

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APPL-NO: JP2000029349

APPL-DATE: February 7, 2000

INT-CL (IPC): C23C018/31

ABSTRACT:

PROBLEM TO BE SOLVED: To provide a plating method capable of industrially widely utilizing a redox electroless plating method having excellent characteristics and to provide a plating soln. precursory suitable for its execution.

SOLUTION: This plating method is the one in which a plating stage, in which the ions of 2nd metal are reduced by reducing force generated in the case the ions of 1st metal composing a redox system are oxidized and are precipitated onto the surface of the object to be plated, is combined with a stage, in which electric current is flowed to a soln. to reduce the ions of 1st metal, and the soln. is activated. As to the plating soln. precursory, for improving its preservable properties, the state of the plating soln. is made into the stable one by which the reduction and precipitation of the ions of 2nd metal do not

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substantially occur.

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CLAIMS

[Claim(s)]

[Claim 1] It is the non-electrolytic-copper plating bath characterized by the aforementioned complexing agent containing titanium ion trivalent in the aforementioned reducing agent including thiourea or its derivative in the non-electrolytic-copper plating bath containing a copper salt, a complexing agent, pH regulator, and a reducing agent.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Industrial Application] This invention relates to improvement of the reducing agent especially contained in such a plating bath about a non-electrolytic-copper plating bath.

[0002]

[Description of the Prior Art] The plating bath for depositing a copper coat with electroless plating mainly contains the minute amount additive of a bath stabilizer or a brightener, including a copper salt, a complexing agent like a tartaric acid or ethylene-diamine-tetraacetic acid (EDTA), a pH regulator like an AMMONIMU salt or a sodium hydroxide, and a reducing agent like formaldehyde.

[0003] since formaldehyde is usually used as a reducing agent as mentioned above -- an electroless-plating reaction -- following -- as shown in formula: $\text{Cu}^{2+} + 2\text{HCHO} + 4\text{OH}^- \rightarrow \text{Cu} + \text{H}_2 + 2\text{H}_2\text{O} + 2\text{HCO}_2^-$, it is a hydrogen generating reaction

[0004]

[Problem(s) to be Solved by the Invention] Since the electroless-plating reaction which uses formaldehyde as a reducing agent as mentioned above is a hydrogen generating reaction, the so-called unusual deposit [say / urging plating growth] tends to produce it by sticking to the portion to which activation of the generated hydrogen is not carried out. Therefore, when such electroless plating is applied to formation of the electric conduction pattern for example, on the circuit board, faults, such as a fall of the precision of a pattern and a short circuit [**** / un-/ between patterns], may be caused.

[0005] Moreover, since a plating reaction does not occur unless the pH value of a plating bath is high when using formaldehyde as a reducing agent, a plating bath will become strong-base liquid. Therefore, when carrying out plating, risk of having said that plating liquid was attached to clothes or a hand, and it went into an eye accidentally follows, and the irritating odor of formaldehyde has been a problem further.

[0006] So, the purpose of this invention is being able to suppress an unusual deposit which was mentioned above and offering the low radio solution copper-plating bath of the danger on work.

[0007]

[Means for Solving the Problem] This invention is turned to the non-electrolytic-copper plating bath containing a copper salt, a complexing agent, pH regulator, and a reducing agent, and it is characterized by a complexing agent containing titanium ion trivalent in a reducing agent including thiourea or its derivative in order to

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solve the technical technical problem mentioned above.

[0008]

[Function] In this invention, the thiourea used as a complexing agent or its derivative is strongly configured with a copper ion, and can perform stable complexing. Therefore, a non-electrolytic-copper plating bath becomes stable, and it is hard coming to generate decomposition.

[0009] Moreover, since trivalent titanium ion is used as a reducing agent, hydrogen generating can be lost in a plating reaction, and a plating reaction can be produced from the acescence in a neutral region also about pH value.

[0010]

[Effect of the Invention] Therefore, since according to this invention there is no hydrogen generating in a plating reaction as mentioned above, an unusual deposit hardly arises. Therefore, it can prevent being able to have a high precision, and being able to form the electric conduction pattern for example, on the circuit board with non-electrolytic-copper plating, and causing faults, such as a short circuit [**** / un-], and, so, can respond now also to a detailed electric conduction pattern.

[0011] Moreover, also on a base weak in alkaline atmosphere, since the pH value of a plating bath is a neutral region from the acescence, while non-electrolytic-copper plating is applicable satisfactory, danger can be reduced on work.

[0012] In addition, about properties acquired by electroless plating carried out using the non-electrolytic-copper plating bath concerning this invention, such as the adhesion of a copper coat, and conductivity, it is checked by experiment that there is almost no difference with the copper coat by the conventional plating bath.

[0013]

[Example] The non-electrolytic-copper plating bath of the following composition was prepared.

[0014]

Citric-acid 3 sodium salt : 0.34 mol/l EDTA and a disodium salt : [0.08 mol/l nitrilotriacetic acid] : A 0.20 mol/l copper chloride : 0.008 mol/l thiourea : A 0.032 mol/l titanium trichloride : 0.04 mol/l -- this plating bath -- 28% aqueous ammonia -- pH 5.0 -- adjusting -- 40-degree C conditions -- plating processing of 1 hour -- SnCl₂ A solution and PdCl₂ the alumina substrate which finished the activation by the solution -- receiving About 0.8-micrometer copper-plating coat was deposited on a deed and this alumina substrate. The result almost equivalent to what an unusual deposit is hardly accepted and is depended on the conventional plating bath also about the adhesion and conductivity was obtained by this copper-plating coat.

[0015] In addition, although the pH value of a plating bath was able to perform desirable plating operation within the limits of 3.0-7.0 especially, by out of range [this], pH 2.5 [for example,], deposit speed was slow, and sufficient plating coat might not be obtained, and the plating bath might become unstable in pH 7.5, and the copper powder might generate during the plating bath. However, these troubles are solvable a little by operating bath temperature and bath composition.

[0016] the example mentioned above -- as a complexing agent -- thiourea CS (NH₂)₂ although used -- tetrapod methylthio urea (CH₃)₂ NCSN (CH₃)₂ etc. -- the equivalent effect was acquired even if it used the derivative

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